

POLYNUCLEAR AROMATIC HYDROCARBON CONTAMINATION IN SEDIMENTS FROM COASTAL WATERS OF SOUTHERN CALIFORNIA

While extensive analyses of the concentrations of trace metals and chlorinated organic compounds (DDTs and PCBs) have been conducted in southern California over the past 17 years, few data are available concerning the contamination of sediments or biota from polynuclear aromatic hydrocarbons (PAHs).

These substances are present in crude oil, fuel oils and crankcase oil, and combustion of this fuel creates contaminated particulates (soot) which falls back on land. Small oil spills in harbors and certain industrial effluents also contribute PAHs to coastal waters. Industrial discharges to sewers lead to elevated concentrations of these compounds in effluents and sludge entering the ocean from municipal outfalls. They are also known to be toxic to marine life as documented in numerous field and laboratory studies of oil pollution (for a review, see Neff and Anderson, 1981).

In this study for the California State Water Resources Control Board (CSWRCB), SCCWRP director Jack Anderson, with Rich Gossett and his staff, measured the concentrations of PAHs in the sediments at 24 sites from Santa Monica Bay to San Diego Bay, in order to provide an overview of PAH contamination in southern California waters. The sampling locations include sites near the mouths of several rivers and marine stations that receive a wide range of contaminant

inputs. The data were evaluated with respect to potential sources of PAHs and the likelihood of the levels of PAH contamination producing an impact on benthic species.

PAH analyses were performed on three replicate samples from each of the 24 stations. The researchers mea-

sured the levels of 43 different PAH compounds, including isomers of naphthalenes and phenanthrenes, which are petroleum-derived compounds. Reported here are both total concentrations of the PAH compounds (Figures 1 and 2) and patterns of distribution of individual compounds (Figure 3).

The lowest, or background, concentrations of PAHs found in this study were about 150 ppb (ng/g dry weight). This concentration was seen at stations 19 and 20 of this survey, which are the SCCWRP reference station at San Mateo Point (R52-60) and the Point Loma outfall station, respectively (Table 1). PAH concentrations can be "normalized" by dividing by the total organic carbon (TOC) content of the sediment. This procedure permits a comparison of the PAH levels among sites with different total organic carbon levels. Normalization to TOC provides an estimate of the amount of organic contaminant in sediment that is likely to leave particles and be transported to animals ("bioavailability"). Sediments with low TOC, such as sand, are less likely to retain the contaminants. When normalized to TOC, the PAH values

COMPOUND #	NAME (No. of isomers)
5	NAPHTHALENE
6	C1-NAPHTHALENES (2)
7	C2-NAPHTHALENES (6)
8	C3-NAPHTHALENES (2)
9	BIPHENYL
10	ACENAPHTHYLENE
11	ACENAPHTHENE
12	FLUORENE
13	PHENANTHRENE
14	C1-PHENANTHRENES (4)
15	C2-PHENANTHRENES (4)
16	C3-PHENANTHRENES (2)
17	ANTHRACENE
18	FLUORANTHENE
19	PYRENE
20	2, 3-BENZOFUORENE
21	BENZ (a) ANTHRACENE
22	CHRYSENE/TRIPHENYLENE
23	BENZOFUORANTHENES
24	BENZO (e) PYRENE
25	BENZO (a) PYRENE
26	PERYLENE
27	9, 10-DIPHENYLANTHRACENE
28	DIBENZ (a, h) ANTHRACENE
29	BENZO (g, h, i) PERYLENE

Table 1. Aromatic Hydrocarbons Shown in Figures 5-9

for San Mateo Point and Point Loma become 13 ug/g TOC (ppm) and 22 ug/g TOC, respectively.

If the remaining contaminated sites are evaluated on a basis of ng/g dry weight, the highly contaminated locations contain PAHs at levels two orders of magnitude higher than the baseline values (Table 2).

Figures 1 and 2 provide an illustration of the total PAH concentrations in the three replicate samples (± 95 percent confidence interval) at all stations. The highest contamination levels, 13 to 16 ppm dry weight, were found at stations in Los Angeles Harbor (station 6) and San Diego Harbor (station 24) (Fig. 1). Stations 3 and 4 are outfall stations (Santa Monica Bay seven-mile and Palos Verdes 7-3). These sites contained about 10 ug PAH/g dry weight, which was similar to the concentration in Queensway Bay at the mouth of the Los Angeles River (station 7). Two other stations in San Diego Bay (22 and 23) contained total PAH concentrations above 5 ug/g. These seven stations seem to be separated from the remaining 17 by about 2 to 4 ug PAH/g dry weight.

Figure 2 illustrates the distribution of TOC-normalized total PAH concentrations and reveals a somewhat different distribution pattern. The same two harbor stations (6 and 24) are still the most contaminated, and stations 7, 22, and 23 are among those sites containing the highest levels. However, due to the higher organic carbon content at outfall stations 3 and 4, these normalized concentrations have decreased to a level observed at several other sites.

Besides measuring total PAH in the samples, Anderson and his associates examined the data for trends in the distribution of specific PAH

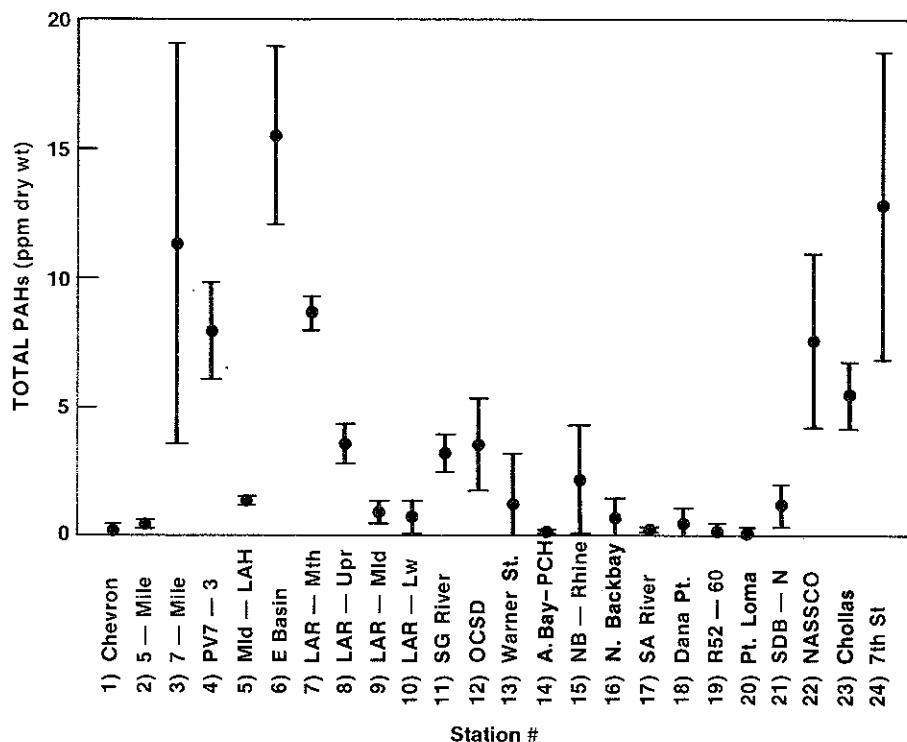


Figure 1. Plot of Total PAHs ($\mu\text{g/g}$ dry weight $\pm 95\%$ confidence limits)

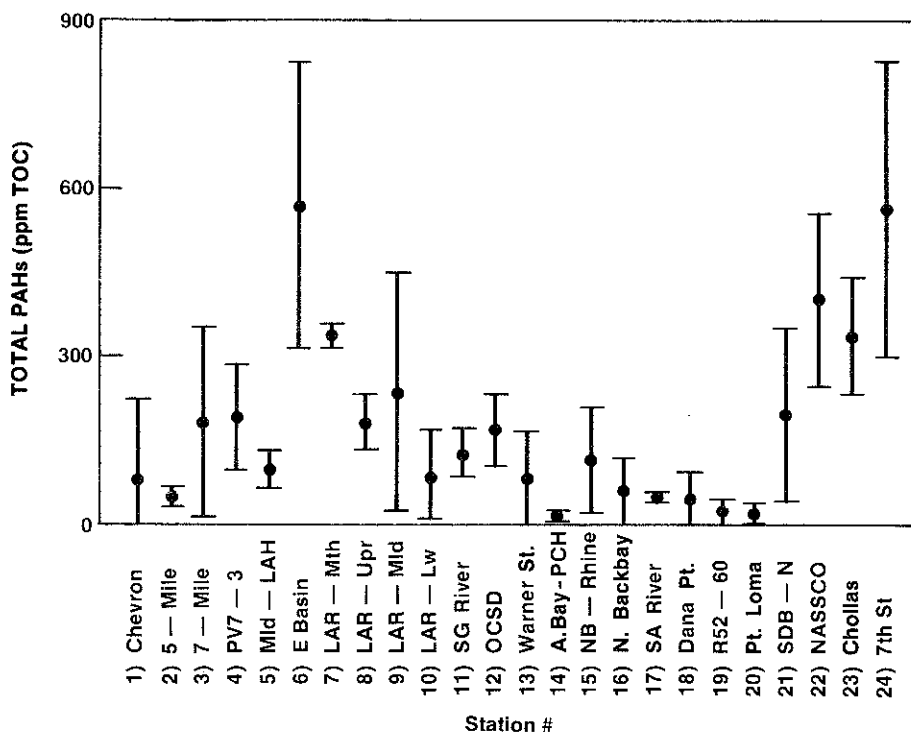


Figure 2. Plot of Total PAHs ($\mu\text{g/g}$ TOC $\pm 95\%$ confidence limits)

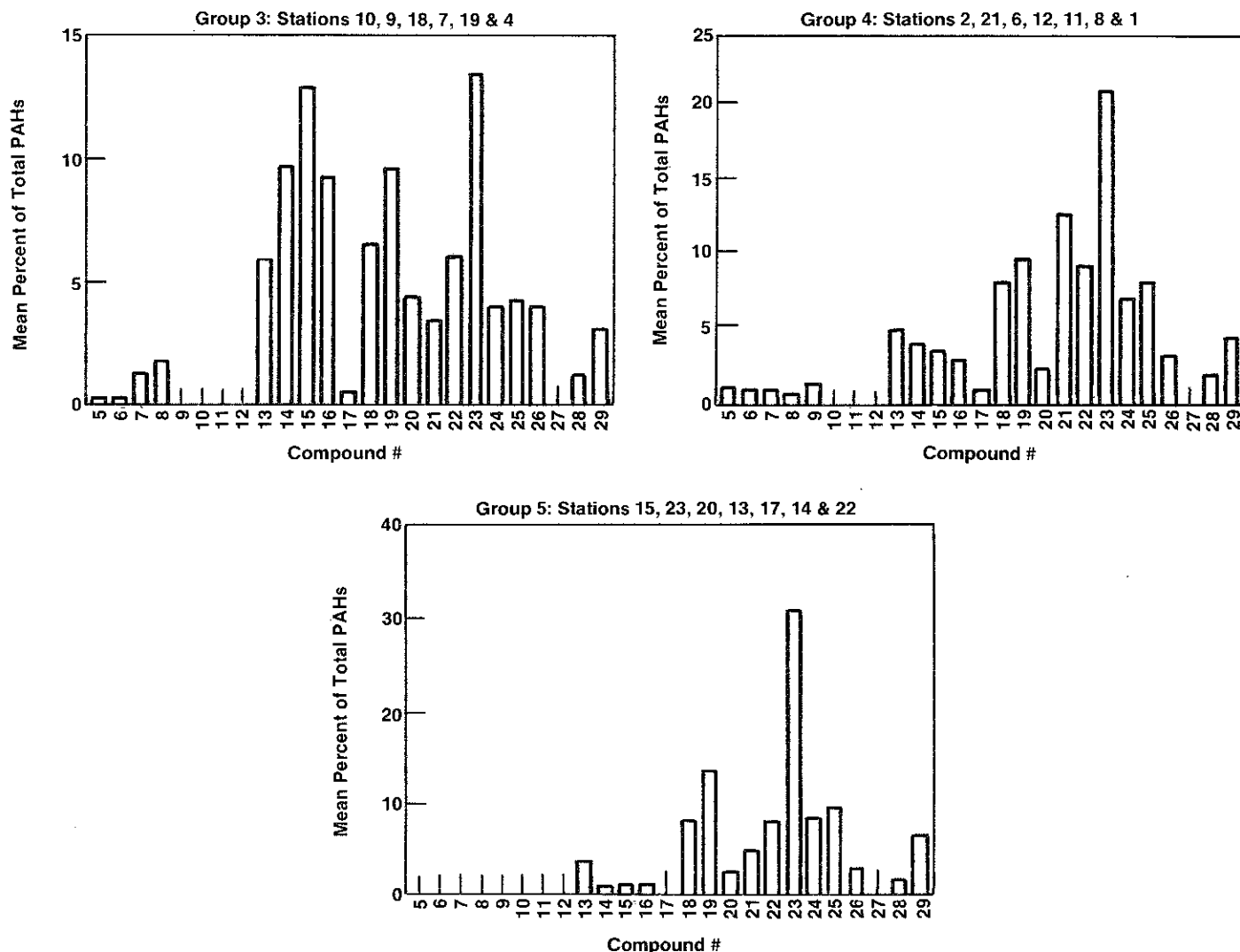


Figure 3. Mean Distribution (%) of Specific PAH in the Three Dominant Groups of Stations.

compounds, in order to help determine sources of the PAH. Figure 3 shows the changes in the composition (mean percentage contribution) of PAH contamination for the three dominant groups of stations. There is a gradual decrease in the percentage contribution of the petroleum-derived PAH compounds referred to as naphthalenes and phenanthrenes (compounds 5-16). The fossil fuel pollution index (FFPI) decreases from group 3 to group 5 stations. Fos-

sil fuel hydrocarbons such as the naphthalenes first disappear from the distribution, as the levels of phenanthrenes (other petroleum compounds) decrease. There is a trend from group 3 to group 5 toward a pyrogenic PAH pattern representing hydrocarbons that have been enhanced through heating or combustion processes. These higher molecular weight compounds are less water soluble and therefore are less bio-

available from sediments, particularly those high in TOC. While active (short term) toxicity is not likely to result from exposure to sediments containing the pattern of group 5, there still could be chronic effects, including mutagenicity and carcinogenicity. Benzo(a)pyrene (compound 25) is one of these compounds that has been shown in numerous tests to produce mutagenicity and carcinogenicity in mammals.

Unlike chlorinated organic contaminants (PCBs and DDTs), PAHs do not accumulate to high levels in fish flesh and are not accumulated by food web transfer. Concern about PAH in the marine environment stems from the concern over effects on populations of marine organisms at polluted sites. Malins et al (1984) has reported PAH levels in Puget Sound ranging from 280 ng/g at a reference site to 63 ug/g at the most contaminated station. Several of the sites contained total PAH levels in the range of 5 to 30 ug/g, comparable to the stations reported in this SCCWRP study.

From examination of the literature on the biological effects of PAH bound to sediment (Anderson and Gossett, 1986), it appears that threshold levels of PAH contamination might be between 5 and 15 ug/g dry weight and around 200 to 500 ug/g TOC. The PAH concentrations of the sediments studied in this project are well within this range and could be expected to have acute or chronic effects on benthic organisms. To avoid the loss of time and make the most cost-effective use of chemical analyses already conducted, Anderson recommends that sediment toxicity testing with selected sediments be initiated as soon as possible.

References

- Anderson, J. W. and R. W. Gossett. 1986. Polynuclear aromatic hydrocarbon contamination in sediments from coastal waters of southern California. Final Report to the Calif. State Water Resources Control Board, Sacramento, CA. 57 pp. and 53 pp. Appendix.
- Malins, D. C., B. B. McCain, D. W. Brown, S. L. Chan, M. S. Myers, J. T. Landahl, P. G. Prohaska, A. J. Friedman, L. D. Rhodes, D. G. Burrows, W. D. Gronlund and H. O. Hodgins. 1984. Chemical pollutants in sediments and diseases of bottom-dwelling fish in Puget Sound, Washington. *Environmental Science and Technology*. 18(9):705-713.
- Neff, J. M. and J. W. Anderson. 1981. Responses of marine animals to petroleum and specific petroleum hydrocarbons. Applied Science Publishers Ltd., London, 177 pp.

Sta.	Location	Mean % dry	Mean % TOC	Total PAH (mean)	
				ng/g dry	ug/g TOC
1	Chevron Outfall	81	0.42	218	76
2	5-Mile Outfall	64	0.79	393	50
3	7-Mile Outfall	22	6.38	11317	190
4	PV Outfall	37	4.28	7902	189
5	Mid-LA Harbor	52	1.45	1384	97
6	LB-Inner Harbor	48	2.78	15470	568
7	LA River Mouth	53	2.56	8599	336
8	Upper LA River	66	1.97	3564	181
9	Mid LA River	82	0.44	892	236
10	Lower LA River	83	1.20	712	83
11	San Gabriel River	43	2.49	3242	131
12	Orange Co. Outfall	65	2.11	3528	182
13	Warner Bridge	66	1.42	1204	76
14	PCH Bridge	72	1.06	165	15
15	Rhine Channel	39	1.86	2208	115
16	Back Bay Newport	49	1.17	706	59
17	Santa Ana River	68	0.56	270	48
18	Dana Pt. Harbor	53	1.13	477	42
19	San Mateo Pt.	58	1.06	142	13
20	Pt. Loma Outfall	64	0.69	154	22
21	San Diego Bay (N)	65	0.62	1205	197
22	San Diego Bay (NASSCO)	43	1.89	7588	401
23	San Diego Bay (Chollas)	49	1.63	5459	336
24	San Diego Bay (7th St.)	50	2.28	12802	562

Table 2. Summary of PAH Analyses for Southern California Sediment Stations